

## Applied Fischer-Tropsch Kinetics for a Flame Sprayed Iron Catalyst

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### INTRODUCTION

There has been a great deal of previous work done of Fischer Tropsch catalysis but until recently, very little rate data have been obtained other than semi-quantitative results. A great deal of the previous literature deals with the proposed and hypothetical mechanisms of Fischer Tropsch catalysis and its similarities/dissimilarities to SNG methanation. Despite the voluminous amount of work in this area there is still controversy as to whether deposited carbon or iron carbide (in the case of iron catalysts) is the active intermediate in the mechanistic scheme.<sup>1</sup> In addition to this there was a great deal of work accomplished at the Bureau of Mines in the 1940's and 50's concerning the behavior of Fischer Tropsch catalysis under various conditions.<sup>2</sup> Iron as well as cobalt and ruthenium have been proposed and studied as possible Fischer Tropsch catalysts.<sup>3, 4</sup> There has also been considerable interest in the incorporation of various promoters in Fischer Tropsch catalysis in order to alter olefin-to-paraffin ratios, minimize CO<sub>2</sub> make, etc. An interesting study being conducted at the University of Utah<sup>5</sup> is seeking to systematically alter various promoters in order to determine the best combination in order to achieve a maximum of C<sub>2</sub>-C<sub>5</sub> hydrocarbons. A short review of Fischer Tropsch technology up to 1975 has been given by Shah and Perrotta.<sup>6</sup>

There have been two kinetic studies using iron catalysts for Fischer Tropsch applications.<sup>7, 8</sup> Dry et. al.<sup>7</sup> used a triple promoted iron catalyst in the pressure range of 10-20 atmospheres and at temperatures from 240-270C to determine the reaction orders of the CO consumption rate with respect to both hydrogen and CO. He employed a differential reactor with H<sub>2</sub>-to-CO ratios varying from 1 to 7. They found that the reaction order with respect to CO was effectively zero but the reaction order with respect to H<sub>2</sub> was first order. Between 225 and 265C they also determined an activation energy of 16.8 Kcal/mole. However all their data were obtained by measurements of the CO<sub>2</sub> and water-make in the exit stream. By assuming that there was minimal oxygenated products (reasonable for iron

catalysts), then the summation of the  $\text{CO}_2$  and water-make should equal the total CO consumption rate. In all cases the ratio of  $\text{CO}_2$ -to-water was less than 1 except at the highest temperatures (265C, where it equaled 1.15). Since the effect of increasing space velocity was to dramatically decrease the  $\text{CO}_2/\text{H}_2\text{O}$  ratio, they concluded that  $\text{CO}_2$  was a secondary reaction produced by the water gas shift reaction. A more recent kinetic study was conducted by Atwood and Bennett.<sup>8</sup> In this case they employed not only a tubular flow reactor but also an internally recirculated reactor (similar to the reactor employed here). They claimed in their paper that there was little difference in the reaction kinetics whether the recirculated reactor or the tubular flow reactor was employed. Based on our experience, it would appear that this was due to their minimal  $\text{H}_2$  consumption ( $\text{H}_2$  in excess) and a zero order dependency of the reaction with respect to CO (as reported by Dry et. al.<sup>7</sup>). In this case they reported that with the iron catalyst, the  $\text{CO}_2/\text{H}_2\text{O}$  ratio was significantly greater than one but it should be pointed out that the temperatures employed in this study ranged from 250C to 315C; that is, significantly higher than the temperatures used by Dry et. al.<sup>7</sup> They proposed a kinetic expression which is based on the rate being dependent on the hydrogen concentration and the fraction of reduced iron present.<sup>9</sup> A psuedo steady state balance between the oxidation of iron by  $\text{H}_2\text{O}$  and its reduction by CO leads to equation (1).

$$r_{\text{CO}} = \frac{k(P_{\text{H}_2})}{1 + b P_{\text{H}_2\text{O}}/P_{\text{CO}}} \quad (1)$$

Experimental data at three temperatures were used to determine the constants  $k$  and  $b$  as a function of temperature. However it should be pointed out that the term involving the ratio of water to CO partial pressures in the denominator was only important for a very few data points. Also, since a constant feed mixture with a  $\text{H}_2$  to CO ratio of 2.0 was used and the authors report that the mole fraction of  $\text{H}_2$  in the product stream was essentially

independent of carbon monoxide conversion, the  $H_2$  partial pressure was close to a constant for all runs. Although the authors show an excellent fit when equation (1) is rearranged to the linear form of equation (2), note that the essentially constant hydrogen partial pressures and a small

$$\frac{P_{H_2}}{r} = \frac{1}{k} + \frac{b}{k} \frac{P_{H_2O}}{P_{CO}} \quad (2)$$

effect of the water-to-CO partial pressure would produce a constant rate at any temperature.

Two other rate expressions based solely on observation, have also been proposed.<sup>9</sup> In one, the rate was observed to depend only on the partial pressure of  $H_2$  (for conversions less than 60%) and, in the other an adequate correlation for cobalt was obtained by equation (3).

$$r_{CO} = \frac{k P_{CO} P_{H_2}^2}{1 + K_1 P_{CO} P_{H_2}^2} \quad (3)$$

Fischer-Tropsch synthesis is highly exothermic and consequently a good deal of attention has been spent on reactor design considerations. Designs ranging from slurry reactors to fluidized beds have been proposed<sup>2</sup> and, in the latter case, actually constructed.<sup>10</sup> It is also common to utilize recycle reactors in order to restrict the temperature rise across the catalyst bed, but a heavy price must be paid in terms of compressor costs. A low pressure drop reactor utilizing parallel plates and inserts coated with catalyst was first proposed by DOE for the exothermic methanation reaction<sup>11</sup> and a similar design using iron catalysts for Fischer Tropsch has been discussed by Haynes, et. al.<sup>12</sup> The work reported here deals with an applied kinetics study utilizing this catalyst concept. While the scope of the project is concerned with product distributions as well as reaction rates, in this paper we will only focus on reactant and make-gas rates.

## EXPERIMENTAL EQUIPMENT AND PROCEDURES

### Berty Reactor System

All of the experiments were conducted in an internally recirculating reactor ("Berty" type) and a schematic of this equipment is shown in Figure 1. Hydrogen and CO are monitored separately via capillary flow meters equipped with pressure drop transducers and the flows are adjusted with the reactor on by-pass to obtain the desired inlet  $H_2$ -to-CO ratio and total flow. Once the desired ratio is obtained, a sample is sent for analysis via gas chromatography using a Carle Model 111 H gas chromatograph. The reactor is then put on stream and the  $H_2$ -CO mix is fed to the reactor. The exit stream leaving the reactor passes first through a "hot trap" (a condenser maintained at 120C) in order to condense waxes. The uncondensed portion of the stream then passes through a cold trap (at 0C) where water and oil are condensed. The gas effluent from this condenser passes into a knock-out pot to remove entrained liquids and then proceeds via a wet test meter to vent. Provisions are made to sample this exit gas stream on line and again, analysis is done via a Carle 111 H gas chromatograph. The reactor pressure is adjusted and maintained by means of a needle valve at the reactor exit. Temperatures within the reactor are measured just above and below the catalyst sample. The mass velocity across the catalyst surface can be adjusted by means of regulating the RPM of the magne drive unit equipped with the Berty reactor. Typically at RPM's above 750 the temperature difference across the catalyst is within 2C and all data reported here were obtained at 1500 RPM.

The Carle Analytical Gas Chromatograph is equipped with an on-line hydrogen transfer tube so that reasonably accurate hydrogen peaks are obtained as part of the analysis. A 2.5 m poropak Q column at 105C was placed in a series-bypass mode with a 2.5 m molecular sieve column maintained at 30C. With the columns connected in series,  $H_2$ , CO and  $CH_4$  pass through the poropak column and into the molecular sieve column where they are temporarily retained. A valve is then switched so that the molecular

sieve is bypassed and  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{C}_2\text{-C}_4$  compounds are separated and analyzed. With the columns placed in series once again, analysis of  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  takes place.

The iron catalyst, supplied by the Pittsburgh Energy Technology Center (PETC) of DOE, consisted of taconite which was plasma-sprayed to an average thickness of 0.56 mm on flat plates of iron substrate. It had a BET area of  $2 \text{ m}^2/\text{gm}$  and a porosity of 0.48. The catalyst assembly consisted of 5 plates, each 7.6 cm high and of varying widths so as to be compatible with the draft tube size of the Berty reactor. The plates were bolted together with two threaded rods and the assembly and dimensions are shown in Figure 2. The catalyst was assembled, leak tested in He and then reduced by heating to  $500^\circ\text{C}$  in flowing  $\text{H}_2$  over a 4-hour period and then holding at  $450^\circ\text{C}$  for 24 hours. Attempts were made to estimate the water make during reduction in order to determine the percentage reduction of the available iron. Unfortunately the slow reduction rate and consequent low  $\text{H}_2\text{O}$  concentrations did not allow for accurate measurements.

The need for a carburization pretreatment when using iron Fischer Tropsch catalysts has been the subject of a number of investigations.<sup>13</sup> In this case we utilized a  $\text{H}_2/\text{CO}$  feed of 1.5 at  $300^\circ\text{C}$  and 1.6 MPa and ran for a total of 30 hours on-stream. This corresponded to the time at which the activity and product distribution stabilized. It should be pointed out however, that the catalyst was idled in  $\text{H}_2$  at  $300^\circ\text{C}$  and 1.6 MPa at the end of each day's running. In addition the conversions varied during this pretreatment and, since the reactor behaves as a CSTR, the catalyst was exposed to varying  $\text{H}_2/\text{CO}$  ratios. This will be discussed below in more detail.

## RESULTS

Prior to entering into a discussion of the results, it is important to emphasize the behavior of a CSTR reactor such as the one used here.

First of all, in discussing reaction rates or product distributions, it is the reactor *exit* conditions which are the independent variables. These are brought about by independent control of the inlet flow rate, inlet composition, reactor pressure, and temperature. Consequently, in the subsequent discussion only the exit conditions will be referred to. Another important factor is that, since a fixed bed catalytic reactor ( $\sim$  plug flow) will have catalyst exposed to both inlet and outlet conditions, it is important to obtain data over a wide range of conversions and inlet compositions. For example, in Fischer-Tropsch synthesis the  $H_2/CO$  ratio will generally increase as conversion increases. Thus it is important to vary the conversion as well as the inlet  $H_2/CO$  ratio so that a wide range of independent data are available for statistical analysis. In this work the CO conversions varied from 15% to 85% and the exit  $H_2/CO$  ratios were varied independently from 0.8 to 18. Total pressures ranged from 0.77 to 3.1 MPa and temperatures from 250C to 300C.

#### Induction Period

The fact that Fischer-Tropsch catalysts generally require an induction (or "carburization") period has already been mentioned. Proper carburization is thought to increase the catalyst lifetime and of course this is exceedingly important for commercial success. In our case, we wished to obtain rate data corresponding to the stable activity of the catalyst and we were unable to run continuously. Because of this latter restriction we followed a procedure of idling the catalyst in  $H_2$  at 1.0 MPa whenever we were not running. Because of these differences we elected to utilize an alternate induction method which was more compatible with our day-to-day operation and which appeared to give the same stable activity<sup>14</sup> as the more typical complex carburization procedure.

The procedure employed during the first 24 hours of induction was to expose the catalyst at 300C and 1.6 MPa pressure to a 1.5  $H_2/CO$  mixture at an "exposure velocity" ( $J$ , volumetric flow rate at standard condition per unit superficial catalyst area) of 2.6 m/hr. Some of the results obtained

during this period are shown in Figure 3. First of all it should be noted that the conversion was very high during the first four hours on stream. This points to the importance of conducting Fischer-Tropsch catalyst screening tests only after the catalysts have been exposed to synthesis gas for at least four hours. Note that during the first 20 hours of induction, the conversion starts off low and builds up during the day's run. It was hypothesized that the H<sub>2</sub> idling procedure was effecting reduction of the active iron carbide so that the first few hours of the run are spent reforming FeC at the expense of hydrocarbon production. As a result, the inlet conditions were changed at 24 hours time-on-stream (TOS) to 3.1 MPa and H<sub>2</sub>/CO = 2.0. As can be seen from Figure 3, once this change was made, the variation in daily conversions was markedly reduced and the catalyst reached apparent stability after about 35 hours TOS.

While the results in Figure 3 show only the total CO conversion, some mention ought to be made of the selectivity to C<sub>5</sub><sup>+</sup> during this period. During the 24 hours TOS, the C<sub>5</sub><sup>+</sup> weight fraction of total hydrocarbon make gradually increased on a daily basis from about 0.05 to 0.20. After this period the fraction remained essentially constant at about 0.25.

#### Product Distribution

In principle either CO<sub>2</sub> or H<sub>2</sub>O can be produced from the chain growth which occurs during Fischer-Tropsch synthesis. However, CO<sub>2</sub> can also be produced via the reversible water gas shift reaction



Typically the CO<sub>2</sub> make was comparable to the CH<sub>4</sub> make at 250C and was 50 to 100% greater than CH<sub>4</sub> at 300C. If the CO<sub>2</sub> is produced from a side reaction such as equation (4), then one would expect an increasing CO/H<sub>2</sub> ratio with increased conversion. As Table I shows, this is indeed the case at both temperatures as long as the H<sub>2</sub>/CO ratio is approximately constant. Also shown in Table I is the equilibrium parameter,  $\phi$ , which is defined as

$$\phi = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{K_{\text{eq}} P_{\text{CO}} P_{\text{H}_2\text{O}}} \quad (5)$$

and will of course be equal to 1.0 at equilibrium ( $K_{eq}$  is the equilibrium constant). It is apparent from the results shown in Table I that the water gas shift reaction is well removed from equilibrium at 250C but closer at 300C. Some measure of the reversible nature of the reaction rate can also be obtained from Table I. That is, at constant conversion the  $CO_2/H_2O$  ratio decreases as the  $H_2/CO$  ratio increases. This would indicate an inhibition of the forward reaction rate of equation (4) by increased product-to-reactant ratios.

Another important aspect of Fischer-Tropsch synthesis is the olefin-to-paraffin ratio of the hydrocarbon products. Table II shows the  $C_2H_4/C_2H_6$  ratio as a function of the  $H_2/CO$  ratio and conversion at two temperatures. Note that this ratio decreases as conversion increases at both temperatures in agreement with Kugler's<sup>15</sup> hypothesis that the main elements in chain growth are olefins, not paraffins. As expected, higher  $H_2/CO$  ratios also lower the  $C_2H_4/C_2H_6$  ratio since these would tend to promote hydrogenation. Comparing the data at two temperatures, it can also be seen that higher  $C_2H_4/C_2H_6$  ratios are favored at the lower temperature.

The experiments conducted during this portion of the investigation were designed primarily to obtain reaction rate data and since a large number of separate runs were required to accomplish this goal, the run times were generally restricted to 3 hours or less. Unfortunately this is not a sufficient length of time to obtain large enough quantities of oil for accurate measurements (the oil make varied from about 0.2 to 4.0 ml/hr). Nevertheless, some insight into the parameters which favor oil make can be obtained from the data shown in Figure 4. Here the weight fraction of  $C_5^+$  ( $C_5^+$ /total hydrocarbon make) is plotted as a function of conversion for different  $H_2/CO$  ratios at 250C. As expected, increasing conversions result in higher  $C_5^+$  fractions (the chain has a chance to grow) and apparently higher  $H_2/CO$  ratios retard the formation of higher carbon numbers. Within the accuracy limitations of the data, the  $C_5^+$  fraction did not appear to be a function of pressure at 250C. However this



was not the case at 300C where it was found that higher pressures tended to increase the  $C_5^+$  fraction. Because of this, there were not enough 300C data at similar conditions in order to obtain a good comparison with the data at 250C. Nevertheless the results in Table III show a definite decrease in the  $C_5^+$  fraction as the temperature increases from 250C to 300C.

Another parameter of interest in Fischer-Tropsch synthesis is the product distribution of the hydrocarbon make. During most runs a small but detectable wax was collected from the hot trap (see Figure 1) but the quantities were too small for accurate analysis. A number of oil-make samples were also subjected to GC-MS analysis and carbon numbers up to about 18 were detected with the highest weight fraction at C8 or C9. The major constituents of the oil were the normal paraffins with varying quantities of olefins and branched compounds at each carbon number. Little in the way of oxygenated compounds were detected.

A common analysis to which Fischer-Tropsch hydrocarbons are subjected is the so called "Schulz-Flory" distribution.<sup>16</sup> In this case the log of the mass fraction of each species divided by its carbon number would plot linearly as a function of carbon number if Fischer-Tropsch synthesis follows equal probability chain growth. Such a plot, typical of the data collected here, is shown in Figure 5. As can be seen, while linear plots are obtained at low and high carbon numbers, there is a transition region between C<sub>4</sub> and C<sub>8</sub> which does not plot linearly. Since the C<sub>1</sub>-C<sub>4</sub> compounds essentially remain in the gas phase and the  $C_5^+$  compounds are collected in the liquid phase, it was first thought that the behavior in Figure 5 was due to a material balance error. However when various arbitrary errors were added, either to the gas or liquid quantities, the same type of plot resulted. Evidently the Schulz-Flory distribution does not apply over the complete carbon number range. It is interesting to note that similar results with this catalyst have been obtained at PETC using a tubular flow reactor.<sup>14</sup>

### Reaction Rates

Ideally we would like to measure intrinsic reaction rates (that is, rates in the absence of all transport limitations) under proposed commercial operating conditions such as those used here. For Fischer-Tropsch synthesis this is difficult to do because of the production of higher carbon number oils which could saturate the catalyst pores and lead to the necessity of gaseous reactants having to diffuse through liquid filled pores. Although the thickness of the catalyst used here was only 0.56 mm, the very low diffusivities of gases in liquids ( $\sim 10^{-5}$  cm<sup>2</sup>/sec) can still result in pore diffusion limited rates. This will be discussed in more detail below. For high reaction rates it is also possible to be limited by gas-solid transport phenomena. This was avoided in these experiments by increasing the reactor impeller speed until there was no separate dependency of the rate on impeller speed. This was found to occur at 750 rpm and, as mentioned earlier, all data were obtained at 1500 rpm.

Because of the possibility of pore diffusion limitations, the rate data were not subjected to thorough evaluations of various mechanistic kinetic expressions. In addition, because of the complexity of Fischer-Tropsch synthesis, it was decided to first attempt to analyze the rate of consumption of CO, independent of the species, produced. Consequently a simple power law model in terms of CO and H<sub>2</sub> partial pressures was evaluated but it did not provide for a sufficiently accurate correlation. Although a number of more complex models were found to give adequate correlations of the data it was found that the rate expression given by equation (1) gave as good a correlation as any. Specifically

$$r_{CO} = \frac{k P_{H_2}}{1 + b P_{H_2O}/P_{CO}} \quad (1)$$

with  $k = 7.6 \times 10^3 \exp \left[ \frac{-8820}{RT} \right] \quad (6)$

$$b = 0.40 \exp \left[ \frac{1430}{RT} \right] \quad (7)$$

In these equations  $r_{CO}$  is expressed in terms of the superficial area of the catalyst, g moles/m<sup>2</sup>-hr, pressure is in atmospheres and temperature is in degrees Kelvin.

In comparing these values with those given previously by Atwood and Bennett<sup>8</sup> for a potassium promoted fused iron catalyst, the major difference is in the apparent activation energy for k. Atwood and Bennet reported a value of 20.3 Kcal/mole whereas we observe a much lower value of 8.8 Kcal/mole. Again this might be due to strong pore diffusion effects since it is well known that for near first order kinetics, pore diffusion rate limitations will produce an apparent activation energy equal to one-half its true value. If this were the case, one would expect that equation (1) would not give as good a fit at the higher temperature. Figure 6 shows a plot of the predicted versus the measured values of  $r_{CO}$  and, as can be seen, the data scatter is definitely larger at 300C. In fact the average deviation at 250C was approximately 10% whereas it was 20% at 300C.

As already mentioned, CH<sub>4</sub> was the most significant product under all conditions. Consequently a separate determination was made of a rate expression which would describe its rate of formation. Due to the fact that CH<sub>4</sub> is only one of many products, no attempt was made to base the rate expression on kinetic mechanisms. Instead a simple power law model was employed and the results are shown in equation (8)

$$r_{CH_4} = 5.7 \times 10^4 \exp \left[ \frac{-13,120}{RT} \right] P_{CO}^{-1/2} P_{H_2} \quad (8)$$

Here again the rate is given in moles/m<sup>2</sup>hr and the pressure in atmospheres. As expected, an increased rate of CH<sub>4</sub> production is favored by higher temperatures and higher H<sub>2</sub>/CO ratios.

A similar attempt was made to obtain a suitable correlation for the rate of CO<sub>2</sub> production. Since it is hypothesized that the CO<sub>2</sub> is produced via the water gas shift reaction, it was anticipated that the rate here would depend on the partial pressures of CO and H<sub>2</sub>O. Surprisingly however,

the rate was found to be independent of  $P_{CO}$  but rather to be dependent on the  $H_2O/H_2$  ratio as shown in equation (9).

$$r_{CO_2} = 6.58 \times 10^7 \exp \left[ \frac{-15,500}{RT} \right] \left( \frac{P_{H_2O}}{P_{H_2}} \right)^{1.3} \quad (9)$$

This could be explained in two ways: the reverse reaction rate is significant and strongly dependent on  $P_{H_2}$ ; and CO is in excess (since  $H_2O$  is a product of the primary synthesis reactions). The first portion of this explanation can not be proven but seems to be reasonable (strong  $H_2$  adsorption could produce the same effect). Although the data used in obtaining equation (9) covered a wide range of CO/ $H_2O$  ratios (0.2-12), there were only three runs (out of 62) with CO/ $H_2O$  less than one. Since these runs had very high  $CO_2$  production rates and high CO conversions, it is conceivable that the rate of  $CO_2$  production does depend on  $P_{CO}$  when it is less than or equal to  $P_{H_2O}$ .

#### Diffusion Limitations

The possibility of strong pore diffusion effects has already been mentioned and the data for the CO consumption rate gives some evidence of its existence. However the rate expression for  $CO_2$  production had an activation energy more typical of kinetic reactions and since it was found to depend on  $P_{H_2O}$ , the primary product of Fischer-Tropsch synthesis, it is somewhat surprising that it did not have a lower apparent activation energy. A possible explanation could be that the dominant reaction is methanation and, if it were much faster and in parallel with the other slower reactions, it could be the only pore diffusion limited reaction. Since equation (1) is based on the total CO consumption rate and  $CH_4$  is the major product, this would explain the apparent discrepancy in the apparent activation energies in equations (6) and (9). Some support of this argument is given by the low activation energy associated with  $CH_4$  production [equation (8)].

Whereas separate experiments to quantify the role of pore diffusion were not conducted, estimates of the effectiveness factor can be made provided there is some knowledge of the value of the effective diffusivity. Atwood and Bennett,<sup>8</sup> assuming that CO diffusion in the liquid filled pores was limiting, used a value of  $1.6 \times 10^{-5}$  cm<sup>2</sup>/sec for a fused iron catalyst. Using this value and rearranging equation (1) to give an effective first order reaction, we estimate the effectiveness factor be about 0.30 at 300 C. Thus it appears that we have strong pore diffusion effects with respect to the CO consumption rate. This is probably due to the high rate of formation of CH<sub>4</sub> which was the major product (selectivity ~ 60%).

#### ACKNOWLEDGE

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TABLE I  
CO<sub>2</sub>/H<sub>2</sub>O MAKE AT TWO TEMPERATURES

	H <sub>2</sub> /CO	X <sub>CO</sub>	CO <sub>2</sub> /H <sub>2</sub> O	φ
250 C	2.24	.26	.14	.004
	2.25	.34	.25	.01
	2.16	.50	.37	.01
	5.9	.79	.42	.016
	8.9	.74	.27	.027
300 C	1.2	.60	1.9	.057
	2.8	.59	1.1	.077
	5.5	.62	0.6	.083
	3.6	.75	1.0	.091
	6.1	.79	1.0	.153
	7.3	.74	0.6	.110
	9.3	.76	0.45	.11

TABLE II  
ETHYLENE/ETHANE MAKE AT TWO TEMPERATURES

	H <sub>2</sub> /CO	X <sub>CO</sub>	C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>
250 C	1.5	.15	.14
	1.2	.21	.13
	2.24	.26	.092
	2.25	.34	.076
	2.16	.50	.050
	5.9	.79	.020
	8.9	.74	.012
300 C	1.05	.26	.096
	1.20	.41	.079
	1.20	.60	.028
	2.80	.59	.023
	5.50	.62	.012
	9.30	.76	.005

TABLE III  
COMPARISON OF C<sub>5</sub><sup>+</sup> FRACTION AT TWO TEMPERATURES

T(C)	X <sub>CO</sub>	H <sub>2</sub> /CO	P <sub>T</sub> (MPa)	C <sub>5</sub> <sup>+</sup> Fraction
250	.50	2.5	1.47	.31
300	.51	1.7	1.47	.12
250	.55	4.0	2.15	.18
300	.58	3.3	2.02	.10
250	.65	6.7	2.84	.13
300	.76	8.3	2.84	.07

FIGURE 1: SCHEMATIC OF EXPERIMENTAL EQUIPMENT

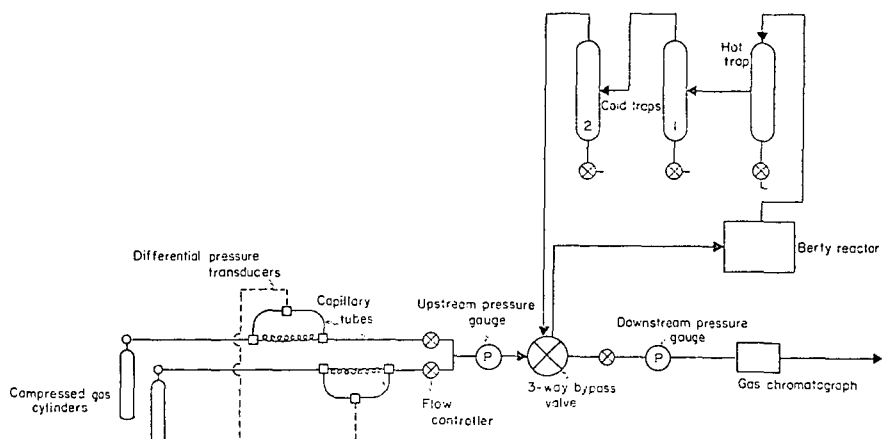


FIGURE 2: CATALYST ASSEMBLY

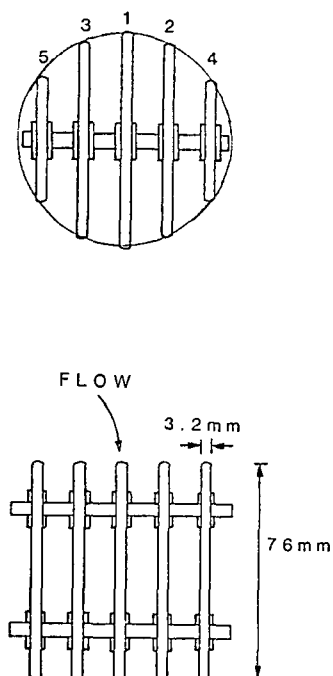




FIGURE 3: INDUCTION PERIOD: CONVERSION VERSUS TIME

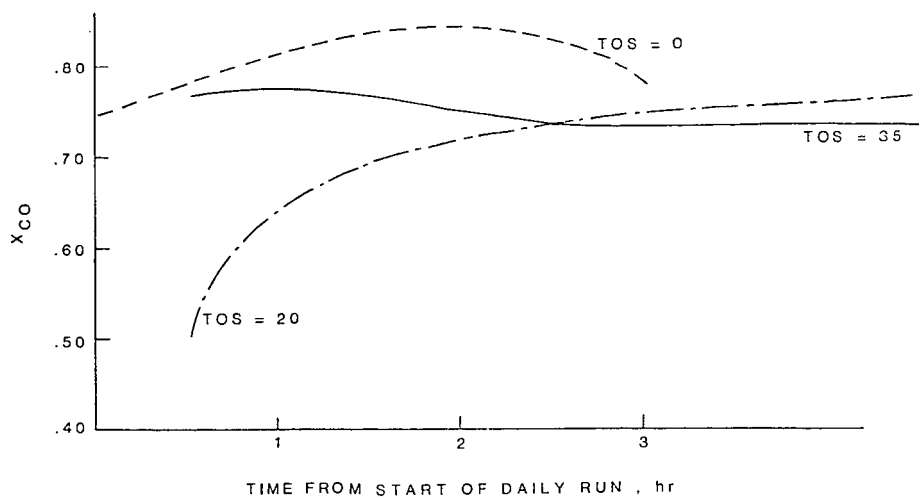


FIGURE 4: WEIGHT FRACTION  $C_5^+$  VS.  $X_{CO}$  (250C)

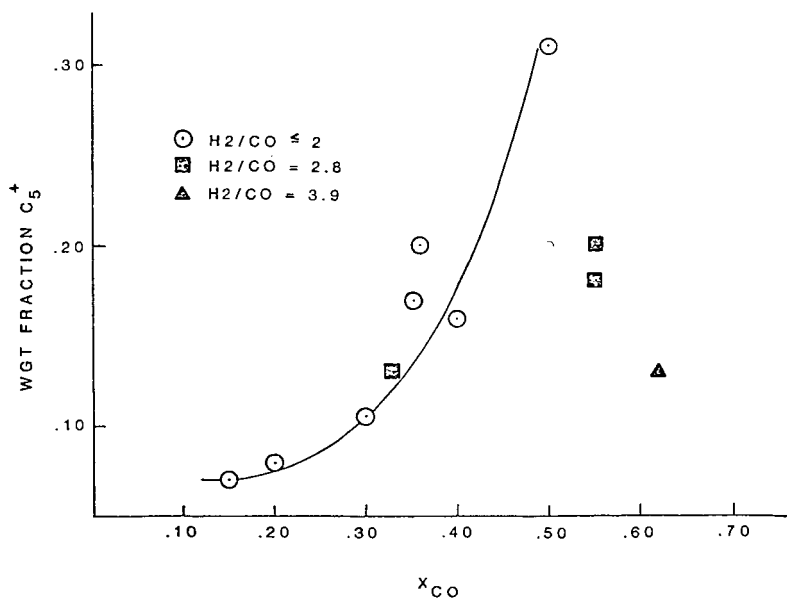


FIGURE 5: TEST OF SCHULZ-FLORY DISTRIBUTION

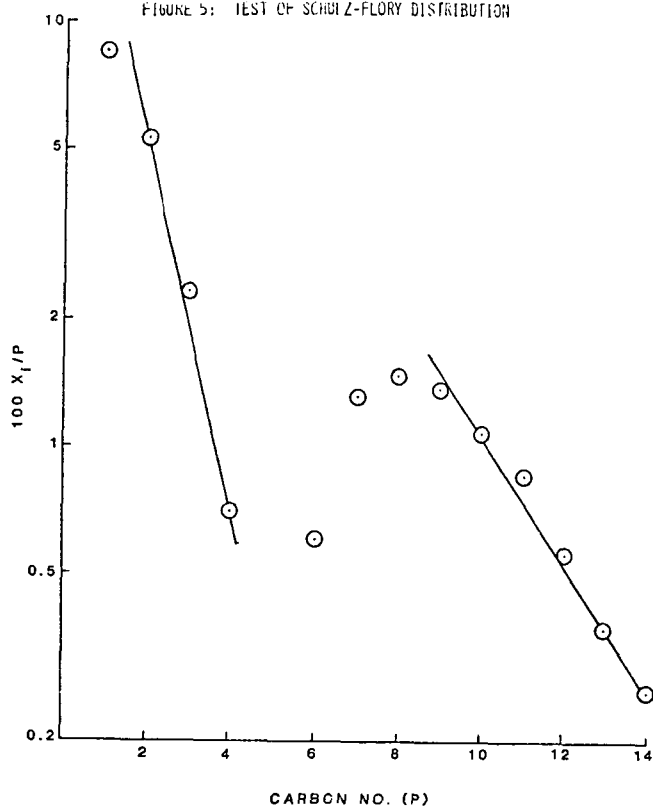


FIGURE 6: PREDICTED VS. MEASURED VALUES OF  $R_{CO}$

